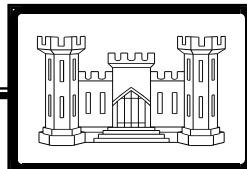


The Missing Link Between DQO's and MQO's

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HTRW Center of Expertise
U.S. Army Corps of Engineers**

12 May 2004



Is Site Contaminated?

Action Level (AL) = 100 ppm

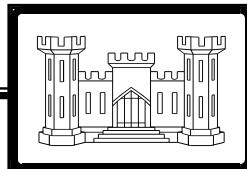
True PCB concentration = 70 ppm

Will correct decision be made based upon some measured value, X?

Yes, if $X = 70 \pm 20$ (50 – 90) ppm.

Maybe not, if $X = 70 \pm 40$ (30 – 110) ppm.

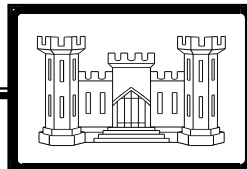
Data Uncertainty \Rightarrow Decision Errors



DQO/MQO Process

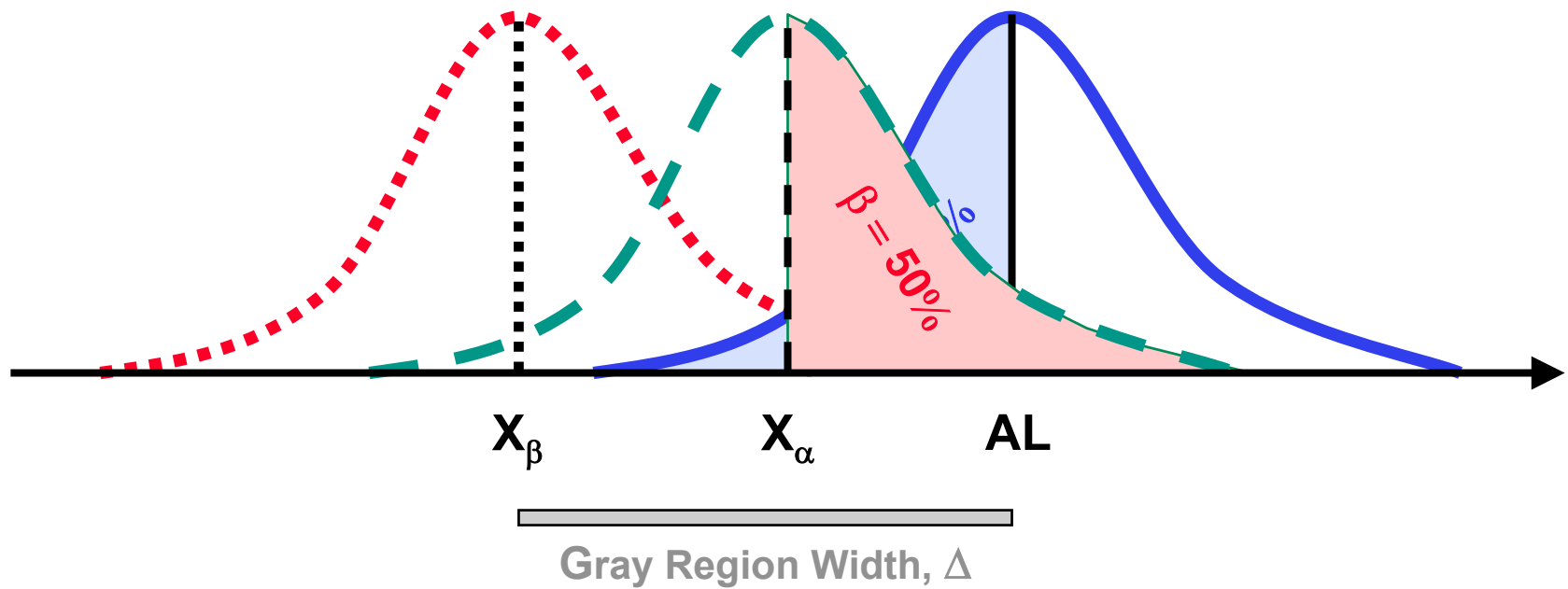
EPA QA/G-4: *“Specify tolerable limits on decision errors which will be used as the basis for establishing the quantity and quality of data needed to support the decision.”*

DQO ? \Rightarrow MQO \Rightarrow Method \Rightarrow Lab

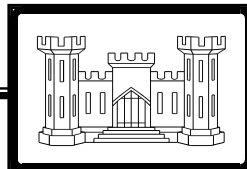


Data Quality and Uncertainty

$H_0: X \geq AL$, $H_A: X < AL$, Decision Errors (α , β)

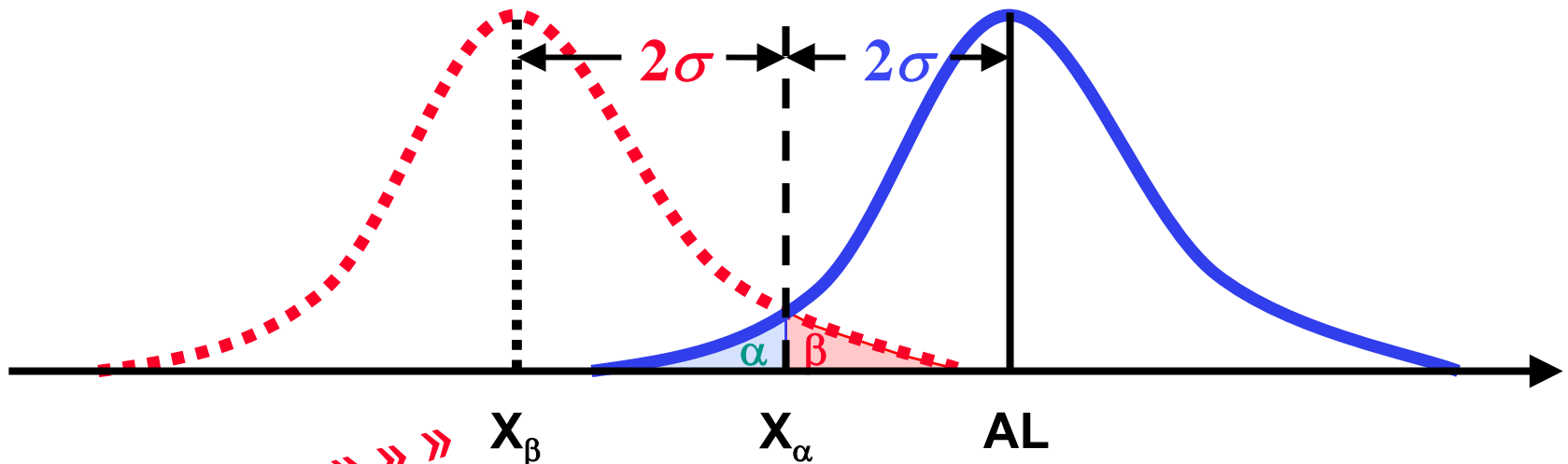


$$\Delta = AL - X_\beta = f(\text{data quality, decision errors})$$



Data Quality and Decision Errors

$H_0: X \geq AL$, $H_A: X < AL$, Decision Errors ($\alpha = \beta = 0.05$)

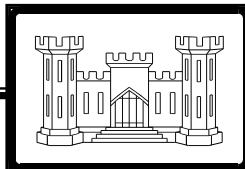


Decision Limit » » »
(DL)

Gray Region Width, Δ

$X_\beta = AL - \Delta = AL - 4\sigma$, where $\sigma = \text{std. dev.}$

Site clean if $X < X_\beta$ but $QL \leq DL = X_\beta$



DQO \Rightarrow MQO

- Requirement: $QL \leq DL(X_\beta)$

- Project Inputs: $DL(X_\beta)$

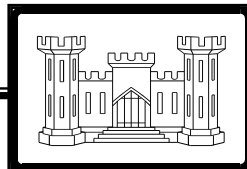
Action Levels (regulatory/background level)

Tolerable Decision Errors (α, β)

- Lab Inputs: QL

Method Detection Limit (MDL)

Data Uncertainty (precision, bias)

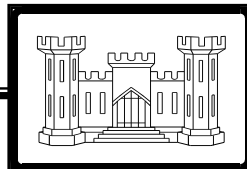


Selection of Contract Labs

- **Total Error (σ)** = $\sqrt{\sigma_{Lab}^2 + \sigma_{Field}^2} \geq \sigma_{Lab} \approx \sigma_{LCS}$
- **Assumptions:** Labs have different performance for precision, bias, and detection limits.

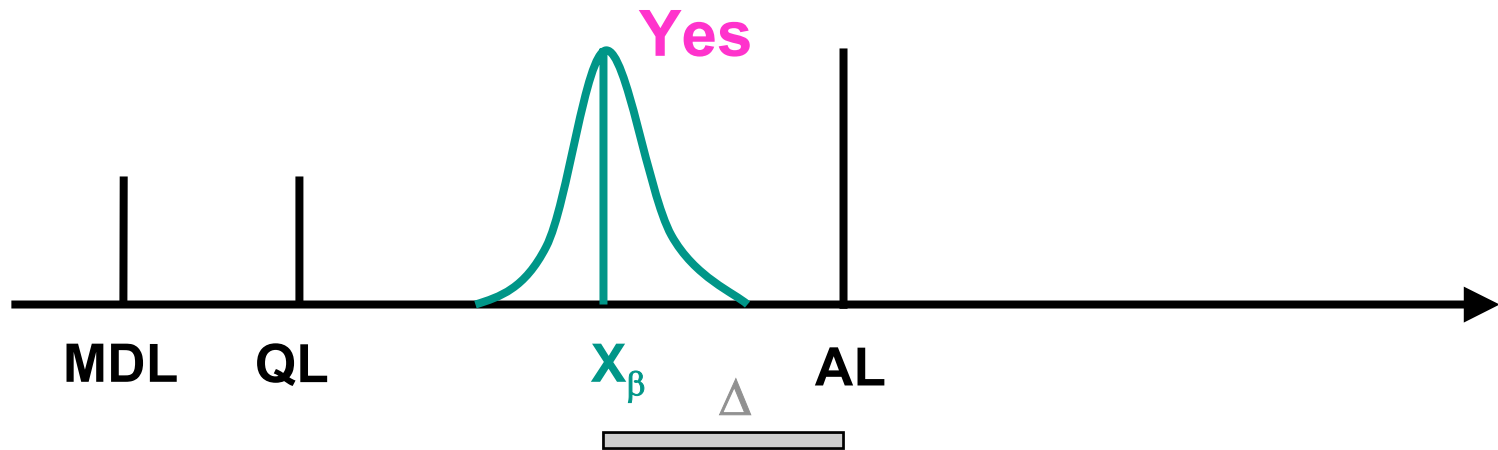
Lab A: MDL = 2 ppb, QL = 10 ppb, σ_{LCS} = 5%. \$\$\$

Lab B: MDL = 4 ppb, QL = 20 ppb, σ_{LCS} = 10%. \$



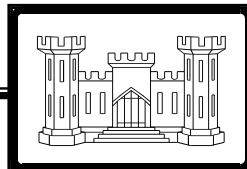
Example 1: Lab A

DQO: Determine if organic contamination is greater than $AL = 30$ ppb with $\alpha = \beta = 0.05$.



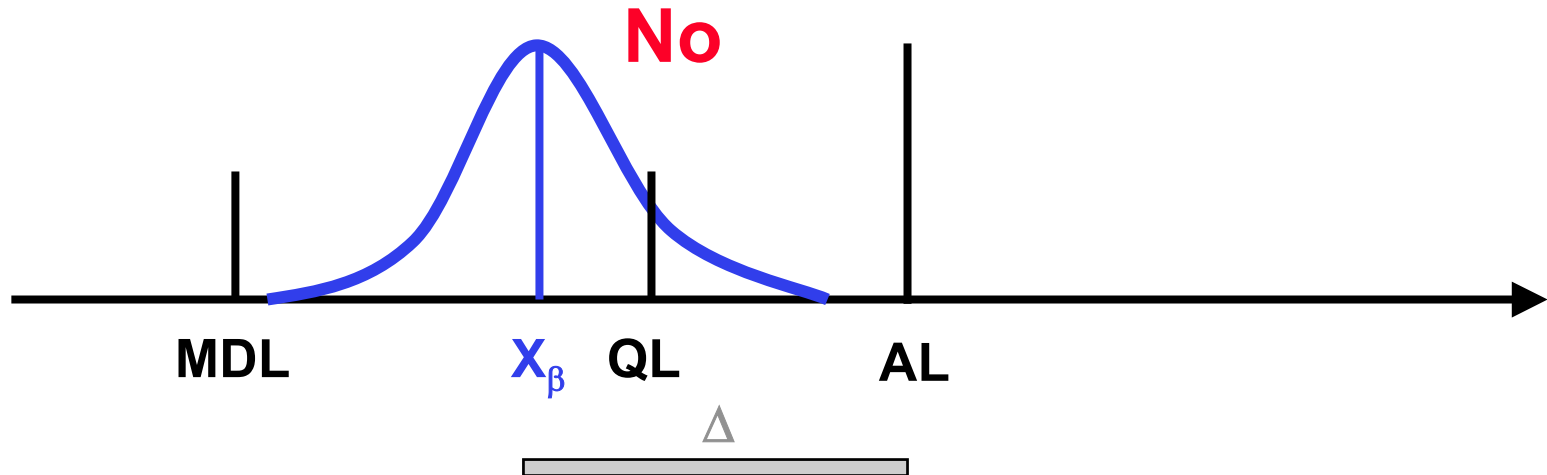
Lab A: $MDL = 2$ ppb, $\sigma_{LCS} = 5\%$. Acceptable?

$$\begin{aligned}
 X_\beta &= AL - \Delta = AL - (4 \times \sigma \times AL) \approx 30 - (4 \times 5\% \times 30) \\
 &= 24 \text{ ppb} > QL = 5 \times MDL = 10 \text{ ppb}
 \end{aligned}$$



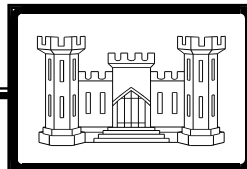
Example 2: Lab B

$AL = 30 \text{ ppb}$, $\alpha = \beta = 0.05$



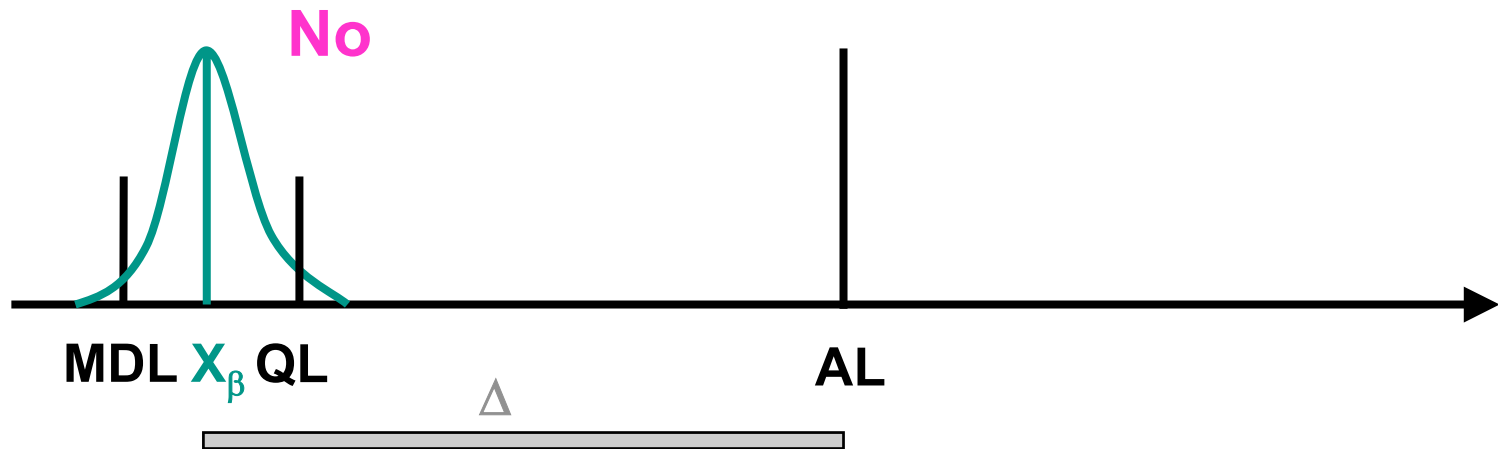
Lab B: $MDL = 4 \text{ ppb}$, $\sigma_{LCS} = 10\%$. Acceptable?

$$X_\beta = 30 - (4 \times 10\% \times 30) = 18 \text{ ppb} < QL = 5 \times 4 = 20 \text{ ppb}$$



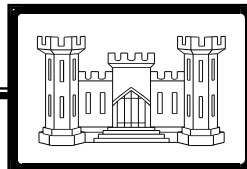
Example 3: Lab A with Large Bias

DQO: Determine if organic contamination is greater than $AL = 30$ ppb with $\alpha = \beta = 0.05$.



Lab A: $MDL = 2$ ppb, $\sigma_{LCS} = 5\%$, $\bar{R} = 30\%$. Acceptable?

$$\begin{aligned}
 X_\beta &= AL - \Delta = AL - (4 \times \sigma \times AL) \approx 30 - (4 \times 5\% \times 30) \\
 &= 24 \text{ ppb} \Rightarrow 7 \text{ ppb} < QL = 5 \times MDL = 10 \text{ ppb}
 \end{aligned}$$



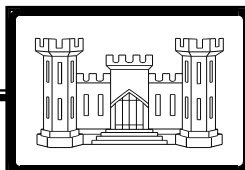
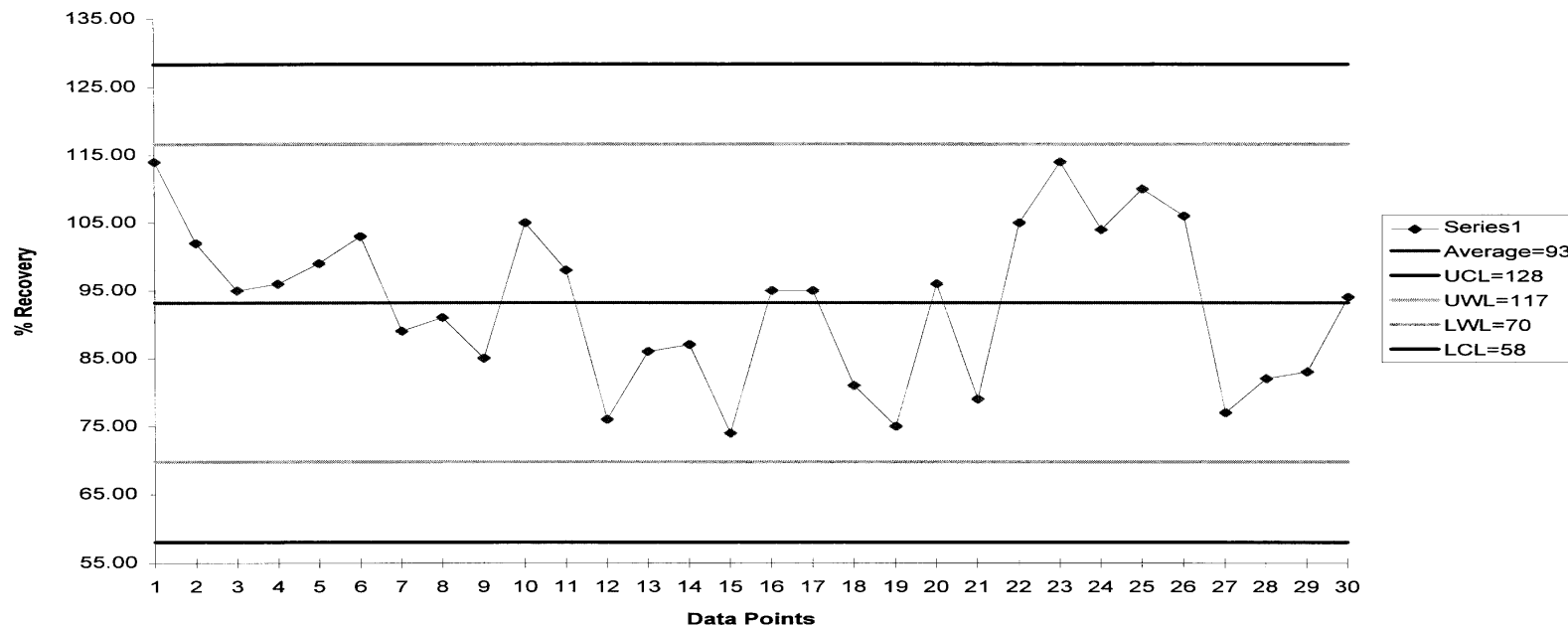
LCS Control Chart (R , σ_R)

Water Matrix

LCS Recoveries

BTEX - 1997

Benzene



Estimated Uncertainty

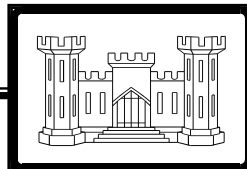
$$U = \frac{C}{\bar{R} / 100} \times \left[1 \pm t \times \frac{\sigma_{LCS}}{\bar{R}} \right]$$

C = measured concentration

\bar{R} = mean %LCS recovery

t = Student's t factor, $t_{(n-1, 1-\alpha/2)}$

σ_{LCS} = standard deviation of \bar{R} (%)



Example: Uncertainty for Ni Data

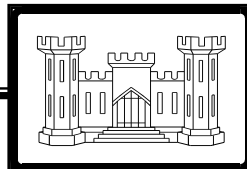
Lab: MDL = 10 ppb, LCS CLs = 75 – 105%.

What is minimum $U_{95\%}$ of Ni at 200 ppb?

$$U_{95\%} = \frac{C}{\bar{R} / 100} \times \left[1 \pm \frac{t \times \sigma_{LCS}}{\bar{R}} \right]$$

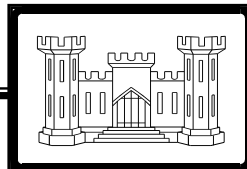
$$\text{CLs} = 90 \pm 15\%, \quad \bar{R} = 90\%, \quad \sigma_{LCS} = 5\%$$

$$\begin{aligned} U_{95\%} &\approx (200 \text{ ppb} / 0.9) \times [1 \pm 2 \times 5\% / 90\%] \\ &\approx 222 \pm 25 \text{ ppb} \end{aligned}$$



Issues or Concerns

- **Bias Correction**
- **Matrix Interferences**
- **Field Errors**
- **Consistent Lab Operations**
- **Regulatory Acceptance**



Summary

- Simple and practical approach for determining the minimum MQOs based on DQOs.
- Useful tool for screening contract labs prior to contract award.
- Estimate the lower bound of laboratory data uncertainty.
- Need consistency in determining and reporting MDL and LCS control limits.
- Need regulatory acceptance.

